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Reaction between Aniline and Chloracetic acid, I.

By

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When 20 c.c. aniline (1.04 mol.) and 20 gm. chloracetic acid (1 mol.) were mixed in a pressure bottle, white sublimate of chloracetanilide was observed to form immediately.¹ The mixture was heated in a boiling water bath for one hour, and the reaction product treated with 250 c.c. water and was left to stand over night at ordinary temperature, and then filtered.

The residue (I) suspended in 50 c.c. water, was digested with conc. ammonium carbonate solution on a water bath, cooled and filtered, the extraction being repeated once more to separate completely the acidic substance from the neutral reaction products.

The combined filtrate, on acidifying with dilute hydrochloric acid, yielded a white precipitate that amounted to 1.5 gm. The substance having been purified, by reprecipitation with hydrochloric acid from its ammonium salt solution, and by recrystallization from the 80 % alcohol solution, melted at 212° and gave on analysis the following results:

- I. 0.1449 gm. substance gave 0.3561 gm. CO₂ and 0.0770 gm. H₂O.
II. 0.1498 gm. „ „ 12.4 c.c. N₂ at 15° and 764.6 m.m.

	Carbon	Hydrogen	Nitrogen
Calc. for C ₁₆ H ₁₆ N ₂ O ₃	67.57	5.68	9.86
Found	67.02	5.95	9.78

¹ P. Meyer, Ber. D. Chem. Ges., 8, 1152 (1875).

The physical and chemical properties of the substance so far as we studied agree with those of phenylimidodiacetic acid mono-anilide which was obtained together with phenylimidodiacetanilide by A. Hausdörfer¹ from the reaction product of phenylimidodiacetic acid and aniline at 170°.

The authors, however, expected that the substance was formed by the interaction of phenylglycine and chloracetanilide. For the purpose of testing this view, an equimolecular mixture of the two substances was heated in a sealed tube in a boiling water bath for one hour and phenylimidodiacetic acid mono anilide was isolated and thus our assumption has been realized.

From the residue (II) insoluble in ammonium carbonate solution, a small quantity of diphenyldiketopiperazine and 1 gm. chloracetanilide were isolated, by extraction of the latter in the cold with 94% alcohol leaving the former compound in the residue. Chloracetanilide thus obtained from the alcoholic solution, was purified by recrystallization from hot aqueous solution, melted at 134° and gave on analysis the following results:

- I. 0.1005 gm. substance gave 0.2108 gm. CO₂ and 0.0479 gm. H₂O.
 II. 0.1523 gm. „ „ 0.1251 gm. AgCl.

	Carbon	Hydrogen	Chlorine
Calc. for C ₈ H ₈ NOCl	56.63	4.75	20.92
Found	57.22	5.20	20.30

The pure diphenyldiketopiperazine, obtained from the insoluble residue in 94% alcohol and purified by the recrystallization from hot alcoholic solution, melted at 263° and gave on analysis the following results:

- I. 0.1462 gm. substance gave 0.3844 gm. CO₂ and 0.0708 gm. H₂O.
 II. 0.1462 gm. „ „ 13.4 c.c. N₂ at 15° and 763.2 m.m.

	Carbon	Hydrogen	Nitrogen
Calc. for C ₁₆ H ₁₄ N ₂ O ₃	72.14	5.30	10.52
Found	71.71	5.44	10.81

The filtrate separated from the residue (I), indicates a strong acidic reaction, was neutralized with ammonia and concentrated under reduced pressure to its half volume. The concentrated solution being alkalined with ammonia the unchanged aniline was extracted with 30 c.c. ether and then acidified with dilute hydrochloric acid. The acid solution was

¹ Ber. D. Chem. Ges., 22, 1795 (1889); 23, 1990 (1890).

treated with 30 c.c. ether, the operation being repeated twice to expel completely phenylimidodiacetic acid, and again neutralized with ammonia water, and concentrated to 50 c.c. under reduced pressure. On standing the concentrated solution, after it was acidified with dilute hydrochloric acid, for one day at ordinary temperature, phenylglycine crystallized out. The yield was 3 gm. It melted at 126–127°, and gave the following analytical results:—

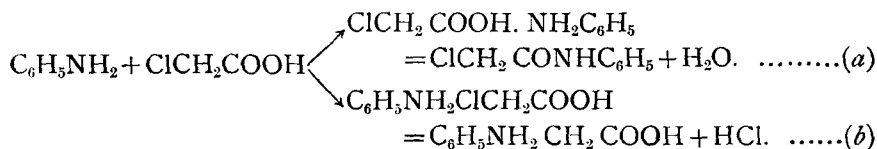
I.	0.2398 gm.	substance	gave	0.5592 gm.	CO ₂	and	0.1310 gr.	H ₂ O.	
II.	0.1560 gm.	„	„	13.55 c.c.	N ₂	at	15°	and	757.8 mm.
				Carbon		Hydrogen		Nitrogen	
	Calc. for	C ₈ H ₉ NO ₂		63.55		6.00		9.27	
	Found			63.60		6.11		9.73	

Distilling off the ether, from the ether extract, there remained 3 gm. phenylimidodiacetic acid¹ which purified by crystallisation from the water solution, melted at 155° and gave on analysis the following results:

I.	0.1838 gm.	substance	gave	0.3870 gm.	CO ₂	and	0.0890 gm.	H ₂ O.	
II.	0.1686 gm.	„	„	9.9 c.c.	N ₂	at	14°	and	762.4 m.m.
				Carbon		Hydrogen		Nitrogen	
	Calc. for	C ₁₀ H ₁₁ NO ₄		57.39		5.30		6.71	
	Found			57.42		5.41		6.94	

Of the reaction products between aniline and chloracetic acid at 100°, we have actually isolated chloracetanilide, diphenyldiketopiperazine, phenylimidodiacetic acid mono-anilide, phenylglycine and phenylimidodiacetic acid.

The chemical reactions involving the synthesis of these substances will be classified in (a) the dehydration and (b) the dehydrochlorination as formulated below:



Hydrochloric acid accelerates the reaction² (a) and on the other hand aniline may produce a similar effect on the reaction (b). Even in the absence of any catalyst, when aniline comes into contact with

¹ P. Meyer, Ber. D. Chem. Ges., 14, 1325 (1881); Hausdörfer, Loc. Cit.

² H. Goldschmidt and C. Wachs, Zs. Physik. Chem., 24, 364 (1897).

chloracetic acid in a sealed tube at 100°, and the reaction is started, one stimulates the other, they will proceed to their equilibrium states. The first reaction which takes place instantaneously after the reacting components are mixed would be easily decided to be (a) by the readiness of formation of the molecular compound. The presence of aniline which is capable forming an addition compound with hydrochloric acid may naturally accelerate the formation of phenylglycine from aniline and chloracetic acid, of phenylimidodiacetic acid from phenylglycine and chloracetic acid. Consequently, chloracetanilide formed as an intermediated product, in the presence of an excess of aniline, without remaining in the reaction products would be entirely transformed into phenylglycineanilide &c. as will seen in A. Hausdörfer's article. Furthermore, aniline plays the same part in the formation of diphenyldiketopiperazine from chloracetanilide and of phenylimidodiacetic acid mono-anilide from chloracetanilide and phenylglycine, as caustic potash does in the formation of the former as observed by Abenius,¹ and also by Prof. Kuhara and Chikashige.²

April, 1922, Laboratory of Organic and Biochemistry.

¹ Ber. D. Chem. Ges., **21**, 1665 (1888).

² Mem. Coll. Sci. Engin. Kyoto, **1**, **1** (1903-8).